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A ^{1}H and ^{13}C NMR Study of Some A3A′3 Spin Molecules Partially Oriented in a Nematic Phase

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The ^{1}H and ^{13}C NMR spectra of some A3A′3 spin molecules dissolved in a nematic phase of EBBA were analyzed. The relative internuclear distances, orientation parameters, and internal motions about the symmetry axes of two methyl groups were obtained and are discussed.

The NMR spectroscopy of molecules in oriented phases has become a useful method for obtaining structural information about molecules in solution since the first observation by Englert and Saupe.$^{1,2)}$ In principle, the orientation parameters and relative distances between spin nuclei in a molecule can be determined by this technique.$^{3)}$ The technique has been applied to many molecules containing various nuclei with internal motions. However, only a few NMR studies have so far been reported concerning molecules containing two methyl groups with internal motions in the oriented phase.$^{4-7)}$ This paper presents the results of our own observations and analyses of the spectra of the substances, which are classified as an A3A′3 spin system, dissolved in a nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA). The relative internuclear distances, orientation parameters, and internal motions about two methyl groups have been obtained and are discussed.

Experimental

Dimethyl sulfide (**1**), dimethyl disulfide (**2**), acetone (**3**), and EBBA were commercial in origin and were used without further purification. The ^{1}H and ^{13}C NMR spectra of **1**, **2**, or **3** in an oriented phase were recorded on a Varian XL-200 spectrometer, operating both at 200 and 50.3 MHz for a 14.6, 15.1, or 14.3 mol% solution in EBBA in a 10-mm tube, respectively. Although there was a slight color change from colorless to yellow upon dissolving **1**, **2**, or **3** in EBBA, respectively, no chemical reactions occurred and the nematic solutions were stable for at least one week during the NMR measurements. The spectra were recorded with 32 K data points using spectral widths of 20000 and 10000 Hz for the cases of ^{1}H and ^{13}C nuclei, respectively. Sixteen FIDs were accumulated without locking for a ^{1}H spectrum, and 5000 FIDs were accumulated with an external D_2O lock for a ^{13}C spectrum. In both cases, the sample was spun in the superconducting system. The probe temperature was about 35 °C. The average line-widths in the nematic phases were about 12 and 8 Hz for ^{1}H and ^{13}C spectra, respectively. Calculations of the spectral and structual analyses were carried out using a HITAC E-600 minicomputer system installed in our laboratory.

Results and Discussion

Analyses of the Spectra. The numberings of the magnetic nuclei in each molecule are shown in Fig. 1. The ^{1}H and ^{13}C NMR spectra of **1** in the nematic phase are given in Figs. 2 and 3. The spectra consisted of 24—28 and 18—20 resolved lines, respectively. Forty-two and forty calculated lines were assigned for the observed ^{1}H and ^{13}C spectra with RMS errors of 0.5 and 1.2 Hz, respectively. The results are given in Table 1. Analyses of the spectra were carried out using a program called LAOCN4D, which was modified from a LAOCN4A program$^{8)}$ while considering dipolar interactions. The indirect coupling constants were cited from reference values$^{9)}$ and were kept constant in the iteration calculation. The errors of the various parameters given in Table 1 correspond to those given from the computer output. The proton NMR spectra of **1**, **2**, or **3** were analyzed as an A3A′3 spin system and the ^{13}C spectra of **1**, **2**, or **3** were analysed as an A3A′3X spin system.

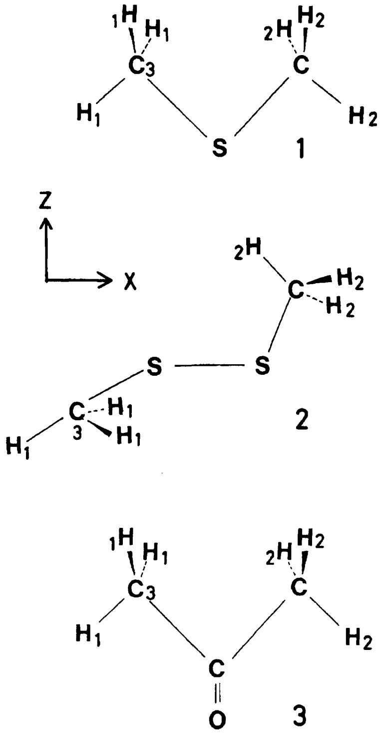

Fig. 1. Numbering systems for **1**, **2**, and **3**.

Table 1. Spectral Parameters for **1**, **2**, and **3** in Hz

Compound	**1**	**2**	**3**
Isotropic phase			
$J(1,2)$[a)]	0.3	0.0	0.55
$J(1,3)$	137.5	140.0	140.0
$J(2,3)$	4.8	0.0	4.0
Nematic phase			
$D(1,1)$	467.3 ± 0.1	60.0 ± 0.1	810.3 ± 0.2
$D(1,2)$	−223.8 ± 0.1	−137.4 ± 0.1	−292.5 ± 0.2
$D(1,3)$	345.6 ± 0.2	63.2 ± 0.2	497.1 ± 0.5
$D(2,3)$	−70.3 ± 0.2	−37.4 ± 0.2	−96.0 ± 0.3

a) Cited from Ref. 9.

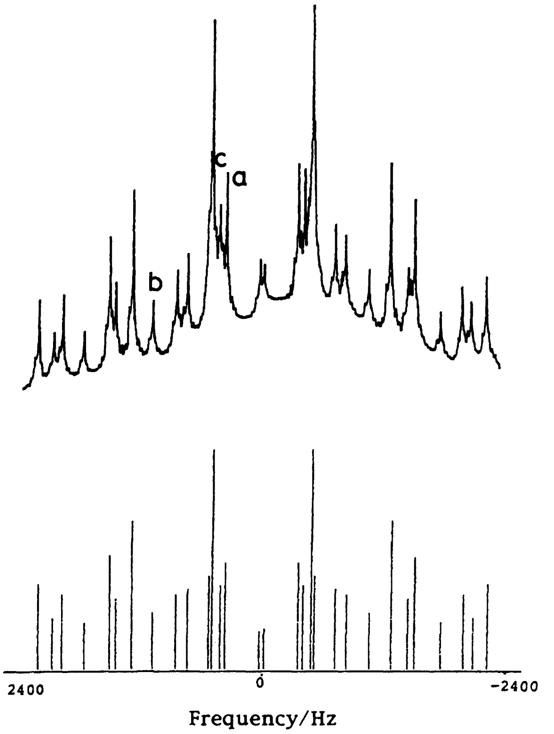

Fig. 2. Observed (upper) and calculated (lower) ^{1}H NMR spectra of **1** dissolved in EBBA at 200 MHz and 24 °C.

The analyses of these spectra were performed in such a way that some specific peaks were characterized using dipole coupling constants.[5)] In Fig. 2 there are three specific peaks which are marked a, b, and c individually. The resonance frequencies of these specific peaks are given by the three following equations:

$$\nu_a = (3/2)D(1,2), \tag{1}$$

$$\nu_b = (9/2)D(1,2) \tag{2}$$

and

$$\nu_c = 3D(1,1) + (9/2)D(1,2). \tag{3}$$

Since we can easily solve the equations, we can obtain $D(1,1)$ and $D(1,2)$. In Fig. 3 there are three specific peaks which are marked d, e, and f individually. The resonance frequencies of these specific peaks are given as the three following equations:

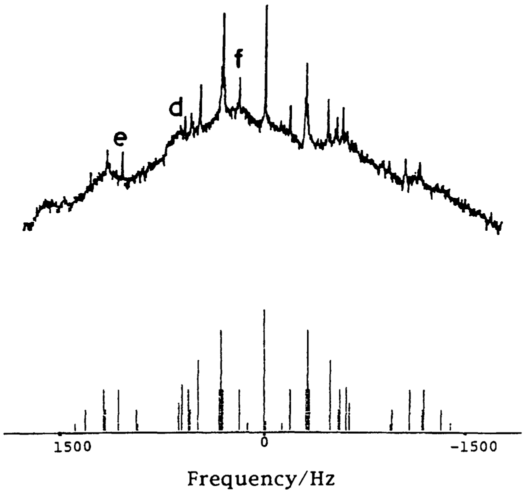

Fig. 3. Observed (upper) and calculated (lower) ^{13}C NMR spectra of **1** dissolved in EBBA at 50.3 MHz and 24 °C.

$$\nu_d = J(1,3) + 2D(1,3) + 2D(2,3), \tag{4}$$

$$\nu_e = (3/2)J(1,3) + 3D(1,3) + D(2,3) \tag{5}$$

and

$$\nu_f = (3/2)J(1,3) + 3D(1,3) + 3D(2,3). \tag{6}$$

We can thus obtain $D(1,3)$ and $D(2,3)$. We can also determine the absolute values of these dipole coupling constants, but not their signs, from the observed spectra. Accordingly, from analyses using LAOCN4D we could show that $D(1,1)$ is not equal in sign to $D(1,2)$, and that the same is true for $D(1,3)$ and $D(2,3)$. Further, we considered that the structure of the methyl group satisfies the following equation:

$$D(1,3)/D(1,1) = 16(\gamma_C/\gamma_H)(\sin^3(\theta_1/2))(2\sin^2(\theta_1/2) - 1), \tag{7}$$

where θ_1 is the angle HCH, and γ is the gyromagnetic ratio.[10)] We can then choose a combination of signs for $D(1,1)$ and $D(1,3)$, because Eq. 7 shows that $D(1,1)$ is equal in sign to $D(1,3)$ and that these signs are positive for the methyl group. We used the Newton–Raphson method to solve Eq. 7.

At last, the ^{1}H and ^{13}C calculated spectra of **1** and **2** are shown in Figs. 2, 3, 4, and 5 with the observed ones, respectively. The ^{1}H and ^{13}C spectra of **3** are similar to those of **1** and are not shown here.

Analyses of the Molecular Structures and Orientation Parameters. The structures of **1**, **2**, and **3** were previously studied by the microwave method (MW).[11—13] The structures are related to Eq. 7, which can be changed to[10]

$$D(1,3)/D(1,1) = (\gamma_C/\gamma_H)(r_{HH}/r_{CH})^3[(r_{HH}/r_{CH})^2-2], \quad (8)$$

with

$$r_{HH}/r_{CH} = 2\sin(\theta_1/2) \quad (9)$$

and

$$\cos^2\theta_2 = 1-(4/3)\sin^2(\theta_1/2), \quad (10)$$

where θ_2 is the angle XCH (X=S or C).

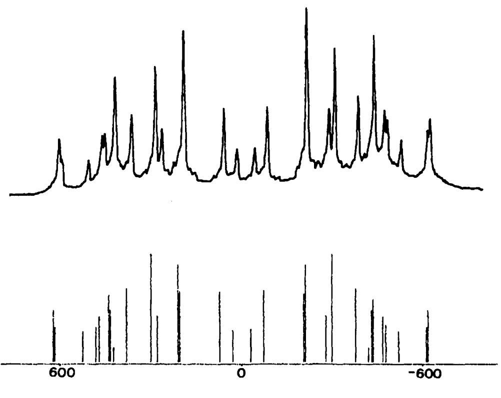

Fig. 4. Observed(upper) and calculated(lower) ^{1}H NMR spectra of **2** dissolved in EBBA at 200 MHz and 24 °C.

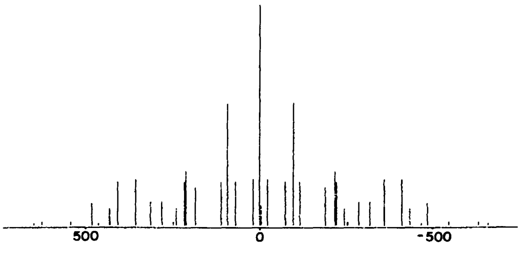

Fig. 5. Observed (upper) and calculated (lower) ^{13}C NMR spectra of **2** dissolved in EBBA at 50.3 MHz and 24°C.

Based on the ratio of $D(1,3)$ and $D(1,1)$ in Eq. 8, the structure of the methyl group can be determined without considering the orientation parameters. Thus, the obtained structural parameters are given in Table 2 as compared with those of the MW method.

We can see that the results of the LC (liquid crystal NMR) method are consistent with those of the MW method concerning **1** and **3**. Concerning **2**, however, we can see a great difference between those obtained by the two methods, LC and MW. This difference is, perhaps, caused by several reasons. First, we ignored any molecular vibration effects in the LC method. However, in a similar case of dimethyl selenide, which is an A3A′3 spin system, there was a difference of 0.3 degrees of the HCH angle in a methyl group between the two analyses with and without vibrational corrections.[7] Therefore, the corrections are not very important. Second, one important reason seems to be due to the structure of **2**. Although **2** is an A3A′3 spin system, as is the others, it doesn't belong to the C_{2v} symmetry group. Since **2** has two sulfur atoms in a molecule, it has a specific dihedral angle. For this reason, **2** is discussed later.

Khetrapal et al. have already discussed the solution structure of **3**.[14] We therefore tried to determine the solution structure of **1**. We have already obtained four direct couplings (Table 1), but couldn't determine the structure of **1** without the following three additional assumptions: (1) First of all, the length of the C–S bond is assumed to be 1.802 Å, which was determined by the MW method. (2) The C_3 rotational axis for the methyl group coincides with the C–S bond. (3) Two methyl groups rotate independently with each other. When these assumptions are considered, we obtain[6]

$$\begin{aligned} D(1,2)/D(1,1) = &-6\sqrt{3}\{S_{xx}\sin^2\theta_1[(\cos\phi-\cos\phi')^2/p^5] \\ &-(S_{xx}+S_{zz})[(\sin\phi-\sin\phi')^2/p^5] \\ &+S_{zz}[\beta^{1/2}+\cos\theta_1[\cos\phi+\cos\phi']^2/p^5]\} \\ &/(S_{xx}\cos^2\theta_1+S_{zz}\sin^2\theta_1), \end{aligned} \quad (11)$$

where $\beta=(2d/r)^2$, r is the rotational radius of the methyl proton and $2d$ is the distance of the two methyl groups in a molecule. Further, $p^2=(\sin^2\theta_1)(\cos\phi-\cos\phi')^2+(\sin\phi-\sin\phi')^2+(\beta^{1/2}+(\cos\theta_1)[\cos\phi+\cos\phi'])^2$, and ϕ and ϕ' are the rotational angles of two methyl

Table 2. Structural Parameters of the Methyl Groups for **1**, **2**, and **3**

	Compound	1	2	3
Method	Item			
LC	r_{HH}/r_{CH}	1.635	1.693	1.608
MW		1.633	1.639	1.625
LC	∠HCH[a]	109.7	115.7	107.1
MW		109.5	110.0	108.6
LC	∠XCH[a]	109.3	102.2	111.8
MW		109.3	108.9	110.3

a) In degree.

Table 3. Orientation Parameters[a)] of **1** and **3** Calculated and Averaged with Decreasing Rotational Angles and Their Temperature Variation

Compound	**1**		**3**	
Parameter	S_{xx}	S_{zz}	S_{xx}	S_{zz}
Angle				
120	0.12158	−0.03685	0.12139	−0.01381
60	0.12199	−0.03658	0.12203	−0.01290
40	0.12200	−0.03657	0.12212	−0.01281
30	0.12200	−0.03657	0.12212	−0.01280
20	0.12200	−0.03657	0.12212	−0.01280
10	0.12200	−0.03657	0.12212	−0.01280
Temperature / °C				
24	0.12200	−0.03657	0.14717	−0.02011
30	0.11536	−0.03466	0.13297	−0.01605
35	0.11040	−0.03297	0.12212	−0.01280

a) Error within 0.0001.

groups, respectively.

Before obtaining the solution of Eq. 11, we tried to clarify the relation between the mutual interaction of two methyl groups and the orientation parameters of the molecules. A program called "*S*-value" was constructed in order to evaluate the orientation parameters based on the observed *D*-values. The calculations were made using following equations:[3)]

$$D_{ij} = -h\gamma_i\gamma_j S_{ij}/(4\pi^2 < {r_{ij}}^3 >) \qquad (12)$$

and

$$S_{ij} = \sum_{p,q} < \cos\theta_p{}^{ij}\cos\theta_q{}^{ij} > S_{pq} \qquad (p,q=x,y,z). \quad (13)$$

Averaging was carried out by rotating the methyl groups around two C_3 axes. For example, if the rotational angle was taken as 120°, nine interproton combinations of two methyl groups were averaged. The number of these combinations increased with decreasing the pitch of the rotational angle. However, the orientation parameters reached constant values with decreasing the rotational angle, as shown in Table 3. In the case of **1**, for example, if the angle became smaller than 40°, the orientation parameters became constant. We can thus see that there is no serious effect of averaging from the methyl-rotational angle if it is less than 40 degree. The critical angle, which is the angle with which the orientation parameters reach a constant value, is dependent on the kinds of molecules, because of the difference in their structures. Finally, averaging was carried out over all conformations with a step of 0.1 degrees.

Based on this information, we solved Eq. 11 using a program called LESSOP (LEast Square Solution of Order Parameters), which was partly modified from the original SHAPE.[15)] The program was applied to an evaluation of the orientation parameters of the molecule, which has the C_{2v} symmetry in the skeleton of the A3A'3 spin system. It was necessary to doubly integrate over ϕ and ϕ'. We used the Romberg integration method to determine the orientation parameters. The results from LESSOP are given in Table 4. Although the CSC angle of the LC method is not consistent with that of the MW method, the angle of the LC method almost coincides with the angle formed with the two C_3 axes of the two methyl groups obtained with the MW method. In the LC method, we solved Eq. 11 so that it depended on the values of $D(1,2)$ and $D(1,1)$. We could therefore determine the angle which consists of two C_3 axes of the methyl groups from Eq. 11, but not the CSC angle.

If the CSC angle is about 99°, which was determined by the MW method, we can estimate the least length between two hydrogens in the two different methyl groups based on the data given in Table 4. It becomes 1.95 Å. This value is less than the 2.26 Å in ethane. Additionally, the potential-energy change about rotation in ethane (2.88 kcal mol^{-1}) is greater than that in **1** (2.18 kcal mol^{-1}).[16)] It is therefore considered that each methyl group rotates freely in **1**. Based on a comparison of **1** and ethane, the two methyl groups of **1** must be more distant from each other. There would therefore be a slight slant of the methyl groups induced from the lone pairs of sulfur, which would be caused by a steric or electronic repulsion among the methyl protons. In **1** there was thus a serious difference between the angle of the CSC and the angle formed from the two C_3 axes of the two methyl groups. We can see the same tendency in dimethyl selenide (**4**) or dimethyl telluride

Table 4. Structure of **1**[a)]

Method	r_{HH}/r_{CH}	∠HCH	∠SCH	∠CSC	r_{CS}
LC	1.635	109.7	109.3	105.0	1.802[b)]
MW	1.633	109.5	109.3	98.8	1.802
				($2x$=104.4[c)])	

a) Bond lengths and angles are given in units of Å and degree. b) Assumed. c) $2x$ is the angle between two C_3 axes of the two methyl groups in a molecule.

Table 5. Structural and Orientation Parameters for the CH_3XCH_3 Type Molecules

Compound	**3**	**1**	**4**[c)]	**5**[c)]
r_{cx}[a)]	1.550	1.802	1.943	2.158
∠CXC[b)]	118.9	105.0	100.85	94.66
S_{xx}	0.14717	0.12200	0.10838	0.04626
S_{zz}	−0.02011	−0.03657	−0.04022	−0.04812

a) The data are arranged with the order of r_{cx} in Å. b) In degree. c) Calculated by LESSOP using the *D* values in Ref. 7.

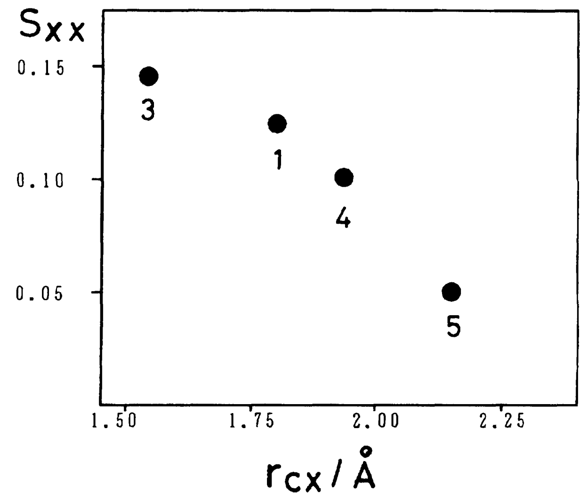

Fig. 6. Structural parameters (r_{cx} in abscissa) vs. orientation parameters (S_{xx} in ordinate).

Table 6. Structural and Orientational Parameters of **2**

Parameter	Calculated	Observed
D(1,1)	60.3(0.41)[a)]	60.0
D(1,2)	−137.0(1.25)	−137.4
D(1,3)	63.1(0.08)	63.2
D(2,3)	−37.3(0.25)	−37.4
<CSSC	84.4	
S_{xx}	0.0783	
S_{zz}	−0.0427	

a) The values in parentheses are the rms error of the calculated ones summed over all conformations with observed one.

(**5**), which has two lone pairs at the center atom like, S (sulfur) in **1**.[7)] However, we can't see such a tendency in **3**, whose center carbon atom doesn't have such a lone pair. In **3**, the angle of CCC is quite consistent with an angle which consists of two C_3 axes of the two methyl groups calculated from the data given in Table 1 by LESSOP.

What factors affect the orientation of the molecules with the CH_3XCH_3 type in the liquid crystal? The data are summarized in Table 5 and are shown in Fig. 6. When the length of the C–X bond (X is the center atom) becomes shorter, both S_{xx} and S_{zz} increase. Additionally, when angle CXC becomes larger, both S_{xx} and S_{zz} increase. It is shown that the orientation parameters are dependent on both the bond length and angle. The length and the angle reflect the size of the molecule. The smaller is the size of the molecule, the better is its orientation in the liquid crystal. A similar tendency appeared in the case of *p*-disubstituted benzenes.[17)] Another factor is the temperature. When the temperature is lowered, S_{xx} of both **1** and **3** increase, as shown in Table 3. This means that the orientation of the longer axis of the molecule along the magnetic field direction is preferred at lower temperatures. This is quite reasonable.

Structural and Orientational Parameters of 2. Dimethyldisulfide (**2**) has a characteristic dihedral angle formed from its skeleton, CSSC. The angle is specific in **2**, and does not appear among the structural parameters of **1**. How does the angle affect the orientational parameters (*S*'s) or the direct spin–spin coupling constants (*D*'s)? Further, **2** has one atom more than those in **1**. Therefore, since the observed *D*'s are limited in number, at least more than three assumptions concerning its structural parameters are necessary for calculations concerning the dihedral angle. The distances of S–S, C–H, and C–S were thus assumed to be 2.022, 1.090, and 1.806 Å, respectively, and the angle of SSC as 104.1° based on electron diffraction data.[18)] The angle of SCH was taken from Table 2 to be 102.2°. The calculations were carried out as follows. A set of three parameters of interest was selected, which is a combination of S_{xx}, S_{zz}, and a dihedral angle. Then, D_{11}, D_{12}, D_{13}, and D_{23} were calculated and compared with the observed ones. This procedure was continued until the rms error between the observed and calculated *D*'s reached a minimum. In the calculations of the *D*'s, the free rotation of the two methyl groups was assumed to be similar to that for **1**. The results are given in Table 6. Among the parameters in Table 6, the dihedral angle was obtained as 84.4° and is compared with that obtained by an electron diffraction (83.9),[18)] microwave (84.7),[12)] or ab initio MO study (87.3—88.4),[19)] respectively.

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